
BIOMATERIALS SCIENCE

An Introduction to Materials in Medicine

Edited by

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TABLE I
Examples of Surface-Modified Bioomaterials[illegible]

GENERAL PRINCIPLES

Surface modifications fall into two categories: (1) chemically or physically altering the atom, compound, or molecule in the existing surface (elemental, existing chemical modification, or (2) overcoating the existing surface with a material having a different composition (coating, grafting, thin film deposition) (Fig. 1). A few general principles provide guidance when undertaking surface modification.

Table Surface Modifications

Interfacial modifications are desirable. The modified zone at the surface of the material should be as thin as possible. Modified surface layers that are too thick can change the prop-

[illegible]

Deinonychus

The surface-modified layer should be the medium to determine the mechanism of the surface modification. This is achieved by carefully studying the modified reaction to the substrate, determining the composition of the substrate, and the surface film at an interfacial zone, incorporating a compatibilizing "primer" layer at the interface, or incorporating appropriate functional groups for strong intermolecular adhesion between a substrate and an overlayer (Chen, 1982).

Surface Remineralization

Such rearrangement occurs quickly. Surface chemistry and substrate state change as a result of the diffusion or translation of surface atoms or molecules in response to the ambient environment (see Chapter 1 and Fig. 2 in that chapter). A new/fresh surface chemistry can migrate from the surface into the bulk, or molecules from the bulk can diffuse to the surface. Such reversal occurs in materials and other thermodynamic systems, as well as in polymer systems. Terms such as "constriction," "dilatation," and "surface segregation" are often used to describe thermally-related alterations in surface structure and chemistry (Kear and Yoon, 1993; Gribshaid et al., 1993; Schemm, 1990, 1991). The driving force for these surface changes is thermodynamic—to minimize the internal surface energy. However, ambident atoms or molecular mobility must exist for the modified change to occur in reasonable periods of time. For a modified surface to remain as it was designed, surface reversal must be prevented or inhibited. This can be done by crosslinking, internally blocking the ability of surface structures to move, or by incorporating a rigid, impermeable layer between the substrate material and the surface modification.

Surface Analysis

Surface analysis is needed. The surface-modified region is usually thin and consists of only minute amounts of material. The low-level contamination can be readily introduced during

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TABLE 2 Physical and Chemical Surface Modification Methods

	Polymer	Matrix	Quemite	Phase
Nonporous castings				
Solvent casting	✓	✓	✓	✓
Lump-in—Bakelite Resin deposition	✓	✓	✓	✓
Surface-active additive	✓	✓	✓	✓
Vapor deposition of carbons and metals	✓	✓	✓	✓
Vapor deposition of tungsten (p-sph/ten)	✓	✓	✓	✓
Conductivity method casting				
Reduction, grafting (chlorine acetone and gamma)	✓	✓	✓	✓
Plasma coating (UV and visible ranges)	✓	✓	✓	✓
Plasma (gas discharge) (O ₂ , nitrogen, argon)	✓	✓	✓	✓
Gas phase deposition				
Ion beam sputtering	✓	✓	✓	✓
Chemical vapor deposition (CVD)	✓	✓	✓	✓
Atomic spray deposition	✓	✓	✓	✓
Chemical grafting (e.g., carboxylic & grafting)	✓	✓	✓	✓
Silicon	✓	✓	✓	✓
Biological modification (Biomimetic immobilization)	✓	✓	✓	✓
Modification of the original surface				
Ion beam etching (e.g., argon, xenon)	✓	✓	✓	✓
Ion beam implantation (e.g., nitrogen)	✓	✓	✓	✓
Plasma etching (e.g., nitrogen, argon, oxygen, water vapor)	✓	✓	✓	✓
Cation exchange (in acid)	✓	✓	✓	✓
Ion exchange	✓	✓	✓	✓
UV irradiation	✓	✓	✓	✓
Chemical reaction				
Thermogravimetric analysis (e.g., cross)	✓	✓	✓	✓
Functional group modification (oxidation, reduction)	✓	✓	✓	✓
Addition reactions (e.g., epoxidation, chlorination)	✓	✓	✓	✓
Conversion catalysis (photocatalytic, autocatalytic)	✓	✓	✓	✓

modification technique. The potential for surface removal to occur during surface modification is also high. The case of corrosion should be understood to ensure that the intended surface is indeed being formed. Since conventional analytical methods are often not sensitive enough to detect surface modifications, special surface analytical tools are called for (Chapter 13).

Comparability

The end products of biomaterials research are devices and materials that are mass produced for use in humans. A surface modification that is too complex will be difficult and expensive to commercialize. It is best to minimize the number of steps in a surface modification process and to design each step to be relatively insensitive to small changes in reaction conditions.

METHODS FOR MODIFYING THE SURFACES OF MATERIALS

General methods to smooth the surfaces of materials are illustrated in Fig. 1, with many examples listed in Table 2. A

low of the more widely used of these methods are briefly described here. Some of the conceptually simpler methods, such as solution casting a polymer on a substrate or metallization by sputtering or thermal evaporation, are not elaborated upon here.

Chemical Reactions

There are hundreds of chemical treatments that can be used to modify the chemistry of a surface. In the context of this design, chemical reactions are those reactions performed without the aid of heat or light. The reactions are performed in the liquid phase, that is, the reactant is in solution with the material, but do not overcoat those areas or molecules with a thin film. Chemical reactions can be classified as nonspecific and specific. Nonspecific reactions have a distribution of different functional groups on the surface. An example of a nonspecific reaction is chemical modification in the phenolic end capping of polystyrene surfaces. Other examples include the covalent linkage modification of materials in dry plasma-frequency glow discharges (AICSD) treatment of materials in oxygen, argon,

electron spectroscopy for elemental analysis (ESCA) (Chilkoti *et al.*, 1991a), chemical derivatization studies (Gomborac and Hoffman, 1988; Glicker and Chaudhry, 1990; Chilkoti *et al.*, 1991a), and static secondary ion mass spectrometry (SIMS) (Chilkoti *et al.*, 1991b, 1992).

11. **Plasma-treated surfaces are available when removed from the reactor, offering an additional advantage for cost-efficient production of medical devices.**

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THE NATURE OF THE PLASMA ENVIRONMENT

Plasma is a thermally and mechanically dissociated gas. Plasma contains a plasma environment contains positive ions, negative ions, free radicals, electrons, atoms, molecules, and photons. Typical conditions within the plasma include an electron energy of 1–10 eV, a gas temperature of 25–60°C, an electron density of 10^{17} to $10^{24}/\text{cm}^3$, and an operating pressure of 0.02–1.0 torr.

A number of processes can occur on the substrate surface that lead to either modification or deposition. First, a concept that takes place between deposition and etching by the high-energy plasma species (ablation) (Yamada, 1977). When sputtering is more rapid than deposition, no deposition will be observed. Because of its complex nature, the ablation or etching process can result in a chemical and morphological change to the substrate.

A number of mechanisms have been postulated for the deposition process. A reactive gaseous environment may create free radicals and other reactive species on the substrate surface that react with other gaseous molecules from the gas phase. Alternatively, reactive small molecules in the gas phase could combine to form highly molecular weight ions or particles that may settle or precipitate onto the surface. More likely, the depositations observed are formed by some combination of these two processes.

PRODUCTION OF PLASMA ENVIRONMENTS FOR DEPOSITION

Many experiments with desubliming both to section on effects and to the substrate onto which the deposition is placed suggest the final outcome of the plasma deposition process (Fig. 3). A diagram of a typical industrially oriented radio-frequency plasma reactor is presented in Fig. 3. The major subsystems that comprise this apparatus are a microwave system (kernel of gas mixing, hot wire, and flow of gas entering the reactor), a vacuum system (maintenance of controlled reactor pressure and inhibition of backstreaming of contaminants from the plasma), an energy system to effectively couple energy into the gas phase within the reactor, and a reactor zone in which the samples are treated. Radio frequency, ionized, or microwave energy can be used in the gas phase. Development for annihilating the molecular weight of the gas phase (species for gas phase destruction), the typical emission from the glowing plasma (spontaneous), and the deposited film thickness (self-sustained), shearing plasma (shearwaves) are also commonly found on plasma reactors.

USED PLASMAS FOR THE IMMOBILIZATION OF MOLECULES

Plasma have often been used to introduce organic metal ions (e.g., zinc, cadmium, mercury) on a surface that can be activated to attach biomolecules (see Chapter 2.11). Certain reactive gas environments can also be used to activate inorganic metal surfaces with organometallic species. For example, a poly-(alkyl-ether glycerol)-poly(ether glycerol) block copolymer, consisting with activity to polymerize with the poly(ether glycerol) block. If the poly(alkyl-ether glycerol) block copolymer is briefly exposed to an argon plasma, the poly(glycerol-ether glycerol) block will be converted (literally) to become an inorganic attachment of pendant poly(alkyl-ether glycerol) chains (Gao *et al.*, 1992).

HIGH-TEMPERATURE AND HIGH-ENERGY PLASMA TREATMENTS

The plasma environments described here are of relatively low energy and low temperature. Consequently, they can be used to deposit organic layers on polymeric or inorganic substrates. Under higher energy conditions, plasmas are effective for etching and ion implantation. In surface modification, ion bombardment and ion implantation may be used to modify the surface of polymers. For example, flame-sprayed degradable materials requiring a high-purity, relatively finely divided (~ 100 nm) material powder form a high-surface plasma or flame. The method is partially patented (see the source and notify negatively for Chapter 2.2 for additional information).

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The proposed chemistry of a typical silane surface modification reaction is illustrated in Fig. 4. Silane reactions can be

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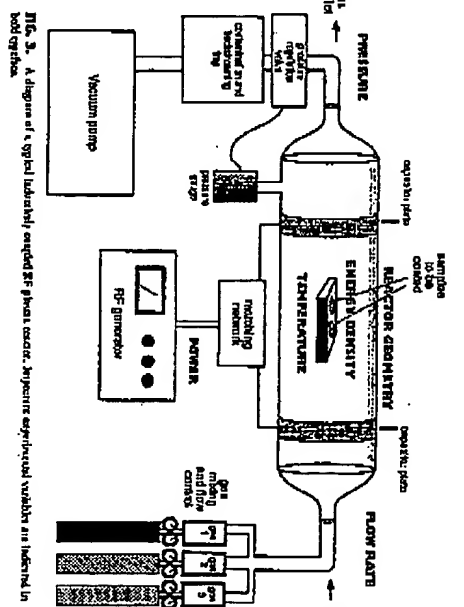


Fig. 3. A diagram of a typical laboratory-coupled RF plasma reactor. Argon gas is introduced into the body of the reactor.

TABLE 4 Summary for Surface Modification of Biomaterials

X = leaving group

$-\text{Cl}$
 $-\text{OCH}_3$
 $-\text{OCH}_2\text{CH}_3$

R = functional group

$-\text{CH}_2\text{CH}_2\text{OH}$
 $-\text{CH}_2\text{CH}_2\text{NH}_2$
 $-(\text{CH}_2)_6\text{C}(\text{CH}_3)_2\text{CH}_3$
 $-(\text{CH}_2)_6\text{O}-\text{C}(=\text{O})-\text{CH}_2-\text{CH}=\text{CH}_2$
 $-\text{CH}_2\text{CH}_2-\text{C}_6\text{H}_5$

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The ion beam method employs accelerated ions with energies ranging from 10^4 to 10^6 eV ($1 \text{ eV} = 1.6 \times 10^{-19} \text{ joules}$) to modify the surface of a material to alter its surface properties. It is largely, but not exclusively, used with organic and inorganic polymers, ions derived from those of the atoms in the periodic table can be implanted, but not all provide beneficial modifications of the surface properties. Important potential

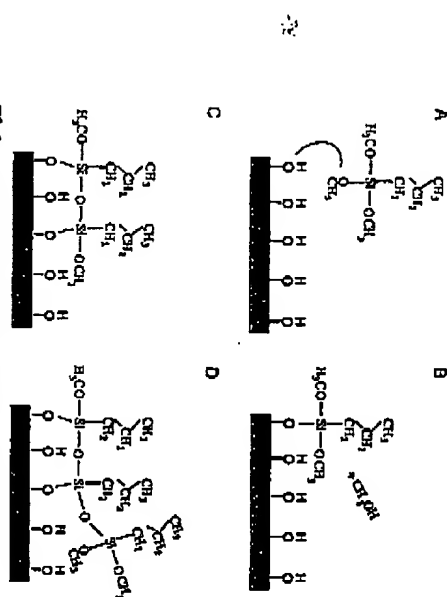


FIG. 4. The chemistry of a) a hydroxylated surface, b) a surface with a hydroxyl group, c) a surface with a hydroxyl group and a methoxy group, and d) a surface with a hydroxyl group and a methoxy group.

application for biomaterials include modification of hardness (wear), lubricity, roughness, corrosion, conductivity, and biocompatibility.

If an ion with an energy greater than a few electron volts hits a surface, the probability that it will enter the surface is high. High energy densities are also transferred to a localized surface zone over short periods. Some considerations for the use of implantation processes are illustrated in Fig. 5. These surface changes must be understood quantitatively for precise engineering of new surface characteristics. Many review articles are available on ion implantation processes for tailoring surface properties (Peters and Papp, 1984; Stohr, 1987).

Specific examples of biomaterials that have been altered by ion implantation processes are plentiful. Bismuth was ion implanted in a Ti-6Al-4V alloy to improve corrosion resistance (Boudreau et al., 1990). Implanting nitrogen into titanium greatly reduces wear (Stohr, 1987). The ion implantation of boron and carbon into type 316L stainless steel improves the high-cycle fatigue life of these alloys (Gibson, 1987).

Langmuir-Blodgett Deposition

The Langmuir-Blodgett deposition method covers a surface with a highly ordered layer. Each of the molecules

that assemble into this layer contains a polar head group and a nonpolar region. The deposition of an LB film using an LB trough is illustrated schematically in Fig. 6. By pulling the vertical plate through the air-water interface, and then pushing the plate down through the interface, leaving the surface film on the air-water interface, compressed as all forces (as illustrated in Fig. 6), multilayer structures can be created. Some components that form organized LB layers are shown in Fig. 7. The advantages of films deposited on surfaces by this method are their high degree of order and uniformity. Also, since a wide range of chemical structures can form LB films, there are many options for incorporating new elements at the surface. The stability of LB films can be improved by crosslinking or polymerizing the molecules together after film formation, often through double bonds in each molecule (Miller et al., 1989). A number of research groups have investigated LB films for biomedical applications (Raymond and Chapman, 1984; Bird et al., 1985; Cho et al., 1990). Many practical reviews on these surface structures are available (Kinsch, 1990; Uman, 1991).

Self-assembled Monolayers

Self-assembled monolayers (SAMs) are surface-coating films that spontaneously form as highly ordered structures (two-

dimensional) crystals on specific substrates (Uman et al., 1988; Uman, 1991; Whiteside et al., 1991). In some ways SAMs resemble LB films, but there are important differences. Examples of SAMs films include *n*-octyl thiolate on hydroxylated silicon (Silber, 1988), alkanethiols on gold (Clegg, 1989), and alkanethiols on silver (Clegg, 1989). SAMs are also used to modify surfaces of polymers, and carbonaceous materials and fibers. Most molecules that form SAMs have the general characteristics illustrated in Fig. 8.

Two processes are particularly important for the formation of SAMs (Uman, 1991): a strong, covalent adsorption of an anchoring chemical group to the surface (typically 30–100 kcal/mol), and van der Waals interaction of the alkyl chains. The strong bonding to the substrate (chemisorption) provides a driving force to fill every site on the surface and to displace contaminants from the surface. This process is analogous to the compression of the LB film by the movable barrier in the trough. Once every adsorption site is filled on the surface, the chains will be sufficiently close together to each other so that the van der Waals interaction forces between chains can exert their influence and lead to a crystallization of the alkyl groups. Molecule mobility is an important consideration in this coating formation process so that (1) the molecules have sufficient time to migrate into position for a tight packing of the chains and groups at the surface and (2) the chains can enter the quasi-crystal. The advantages of SAMs are their ease of formation, their chemical stability (often considerably higher than comparable LB films), and the many options for designing the functional

group that interfaces with the world. Although the discovery of SAMs is relatively recent, biomaterials applications have already been suggested (Kawakami et al., 1989; Prime and Whiteside, 1991).

Surface-Modifying Additives

Certain components can be added in low concentrations to a material during fabrication and will spontaneously migrate to and dominate the surface (Ward, 1989). These surface-modifying additives (SMA)s are well known for both organic and inorganic systems. The driving force to concentrate the SMA to the surface after leaving the SMA with a biomaterial is the surface energy (the bulk material) is energetic—the SMA should reduce the interfacial energy. To do this, two factors must be taken into consideration. First, the magnitude of the difference in interfacial energy between the system with and without the additive and the same system with the SMA at the surface will determine the strength of the driving force leading to a SMA-dominated surface. Second, the mobility of the bulk material and the SMA additive molecules within the bulk will determine the rate at which the SMA reaches the surface, or if it will get there at all. An additional concern is the durability and stability of the SMA at the surface.

A typical SMA designed to alter the surface properties of a polymeric material will be a relatively low-molecular-weight alkylsilane copolymer (see Chapter 2.3). The "X" block will be soluble in, or compatible with, the bulk material; thus

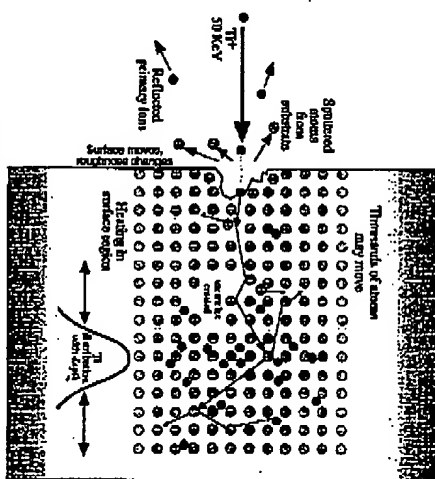


FIG. 5. Some considerations for the ion implantation process.

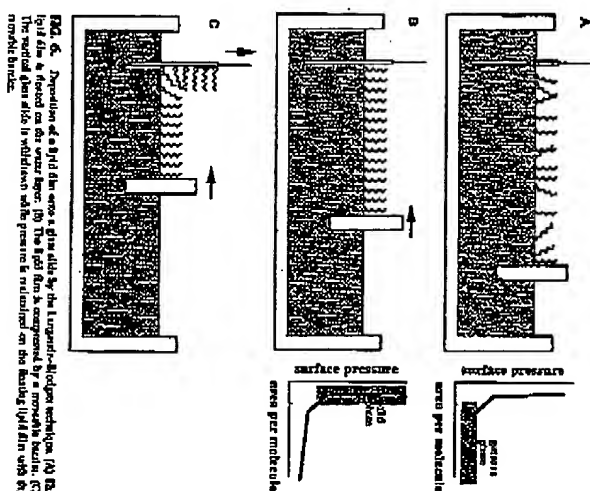


FIG. 2. Dependence of a lipid film on the Langmuir-Blodgett technique. (A) The lipid film is formed on the water layer. (B) The lipid film is transferred by a movable bar. (C) The surface film side is withdrawn with the pressure is maintained on the heating liquid film with the movable bar.

which the SMA is being added. The "A" block will be incorporated with the lipid material and have lower surface energy. Thus, the A block will anchor the B block and the material to be modified at the interface. This is suggested schematically in Fig. 9. During initial formation, the SMA might be distributed uniformly throughout the bulk. After a period for curing or an annealing step, the SMA will migrate to the surface.

For example, an SMA for a polyurethane might have a low-molecular-weight polyurethane A block and a polydimethyl siloxane (PDMS) B block. The A block will anchor the SMA in the polyurethane bulk, the polyurethane A block should be reasonably compatible with the bulk polyurethane, while the low-surface-energy, highly flexible, siloxane B block will be exposed at the air/surface interface. The A block energy (from the air) is hydrophobic. The A block anchor should confer stability to the system. However, if the system is placed in an aqueous environment, a low-surface-energy (in air) polymer (the B block) is now in contact with water—a high interfacial energy situation. If the system,

after fabrication, still exhibits sufficient chain mobility, it might phase-separate to bring the bulk polyurethane on the A block to the surface. Unless the system is specifically engineered to do such a surface phase reversal, this inversion is undesirable. Proper choice of the bulk polymer and the A block can improve surface phase inversion.

Many SMAs for inorganic oxides are known. For example, very small quantities of added will completely alter the structure of a silicon (111) surface (Pfeiffer and Ching, 1987). Copper will segregate at the surface of gold alloy (Trenkle et al., 1988). Also, in molten steel, chromium will concentrate (at the oxide) in the surface, imparting corrosion resistance.

There are a number of additives that spontaneously surface concentrate, but are not necessarily designed as SMAs. A few examples for polymers include PDMS, some extensional liquid (Hansen, 1993), and some UV stabilizers (Yip et al., 1992). The presence of such additives at the surface of a polymer may be unexpected and they will not necessarily form stable, durable surface layers.

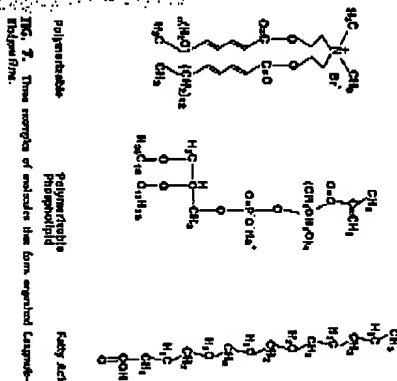


FIG. 3. Three examples of molecules that form organized Langmuir-Blodgett films.

Conversion Coatings

Conversion coatings modify the surface of a metal, like a dense oxide-rich layer that imparts corrosion protection, enhanced adhesion, and sometimes lubricity to the metal. Small is frequently phosphated (reacted with phosphoric acid) or chromated (with chromic acid). Aluminum is electrochemically

Plasma Coating

Teflon (polytetrafluoroethylene) coatings occupy a unique niche in the surface modification literature because of their frequent application and the good quality of the thin film coatings formed (Lueb et al., 1977; Nishida et al., 1984). The deposition method is also unique and involves the formation of a

modified in electronic, optical, or surface field properties. Another reason may also be useful for surface-modifying stainless steel and Ti-6Al-4V alloys (Fineman, 1990; Kierma and Lamm, 1981).

The conversion of metallic surfaces to "oxide-like" electrochemically passive states is a common practice for base-metal alloy systems used as biomaterials. Standard and recommended techniques have been published (e.g., ASTM F46) and are relevant for most non-noble metal base-bearing surgical implants. The hydrolytic degradation of these types of surface passivation techniques has been examined (Neh

Reum, 1986).

Base-metal alloy systems, in general, are subject to electrochemical corrosion ($M \rightarrow M^{+} + e^{-}$) within active corrosion elements. The rate of this corrosion process is reduced 10⁻¹⁰ times by the presence of a naturally conductive, relatively inert oxide surface. For many metallic devices, exposure to a neutral salt (e.g., saline acid in water) for up to 30 min will provide a passivated surface (i.e., protected by its own oxide).

The reason that many of these surface modifications are called "oxide-like" is that the structure is complex, including OH, H, and anions that may or may not be crystalline. Since most passive surfaces are thin films (50–5000 × 10⁻⁶ cm), and are transparent or metallic in color, the surface appears similar before and after passivation. Further details on surfaces of this type can be found in Chapters 12, 22, and 63.

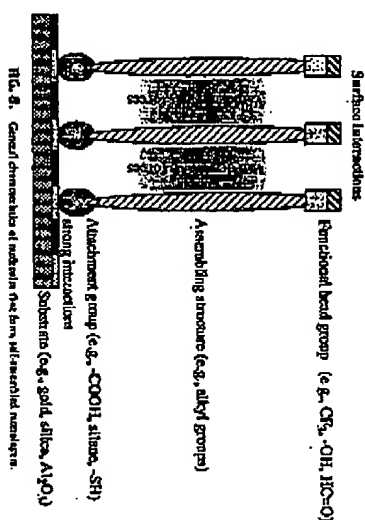


FIG. 4. General description of molecules in the film self-assembly.

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2.10 FABRICS

Shalaby W. Shalaby

The use of fabrics and other fibrous forms as biomaterials dates back to the early Egyptians and Indians. Linen sutures and strips was used by the Egyptians with natural adhesives to draw the edges of wounds together to achieve proper healing and retention of original strength. The American Indians used horsehair, cotton, and thin leather strips (Shalaby, 1985) for a similar purpose. More recent use of fabrics as biomaterials was generally viewed as an extended application of the traditional woven and knitted forms of textiles. Prior to the development of the polyethylene terephthalate-based vascular grafts (Hoffman, 1977; Williams and Roaf, 1973), woven, nonwoven and knitted cellulosic fabrics represented the major types of fibrous materials used by the health care industry. Over the past few decades, with the development of sophisticated polymer and fiber processing technologies, nontraditional forms of fabrics, and fabriclike fibrous products have become available and used successfully as biomaterials in old and new applications (Boretos and Edeen, 1984). Hence, it is an objective of this chapter to survey the major traditional and nontraditional forms of fabric constructions and related products and provide brief descriptions of the constituent materials, their processing and properties. A list of physical and biological characterization and test methods is also provided.

TYPES OF FABRICS AND THEIR CONSTRUCTION

Textile fabrics of woven, nonwoven, and knitted types have been used in one or more biomedical applications. These fabrics are made from a wide range of natural and synthetic fibers, as described in fiber and textile science publications (Joseph, 1981, 1984; Labarthe, 1975; Moncrieff, 1975). Descriptions of these fibers and their parent polymers are given in Tables 1-A to 1-C. The processing and characterization of fabrics are addressed in detail in these publications. In a review of fibrous materials for biomedical applications by Shalaby (1985), major types of materials were highlighted. The formation and characterization of unconventional constructions (some of which are not assembled by fiber processing), such as expanded porous poly(tetrafluoroethylene) (Gore-Tex, W. L. Gore and Assoc., Inc.) and hollow fibers, are discussed in a few reviews (Collier, 1970; Hoffman, 1977; Shalaby, 1985; Shalaby *et al.*, 1984). The characterization and testing of fibrous devices and fabric surfaces have been reported in a few reviews (Cooper and Peppas, 1982; Hoffman, 1977; Hastings and Williams, 1980). Important aspects of these constructions are outlined in Table 2.

Cellulose fibers from cotton or wood pulp are the natural fibers most commonly used in the production of biomedical fabrics and related construction. Highly absorbent cellulose fibers, obtained in recent years by fermentation, may find use in certain sanitary products such as napkins. The small production of these fibers, however, may limit their application. Although cellulose acetate and viscose rayon are less commonly used as fibers than cellulose, interest in other regenerated natu-

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